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Effect of Similarity of Particles on Gas Kinetic Quantities with Application to Nuclear Spins

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In this paper the effect of similarity of particles on gas kinetic quantities (coefficient of viscosity, thermal conductivity, and diffusion) is studied. The symmetrization of the wave function is complicated by the presence of all degrees of freedom which though dynamically unimportant distinguish the particles from each other (orientation of the angular momentum of rotation, electronic and nuclear spins). The theory is applied in detail to the determination of the coefficient of viscosity and thermal conductivity of the *ortho-* and *para*-modifications of hydrogen. Marked differences are predicted depending upon the relative concentration of the *ortho-para* forms. Evaluation of so far uninterpreted measurements of thermal conductivity coefficients lead to good agreement with the theoretically predicted values. It is furthermore found that in the determination of the coefficient of diffusion no symmetrization of the wave functions has to enter. The theory allows in certain favorable cases a determination of nuclear spins of isotopes from viscosity observations, the method being independent of a possibly present magnetic moment. As an experimentally promising example the case of neon is calculated in detail.

INTRODUCTION

It has been shown by Massey and Mohr[2] that the wave mechanics of collisions has to be taken into account in kinetic theory calculations of the coefficients of transport phenomena. An interesting feature of these calculations is the part depending on the symmetry of the colliding particles. If a gas consists of molecules which are identical in the sense of quantum theory then the principle of exchange will operate at every molecular encounter.

Massey and Mohr assumed that two colliding atoms or molecules being neutral particles are in all cases to be described by eigenfunctions which are symmetrical in the coordinates defining the distance between the centers of gravity of the atoms (molecules). They therefore describe uniformly the collisions between helium atoms and between hydrogen molecules. It is at this point that in our opinion an important change and refinement of the theory has to be introduced. In most actual gases owing to the presence of spin states of the electrons and the nuclei, excited states, *ortho-* and *para*-states, or isotopies, the molecules are not all identical and consequently the exchange principle will apply only to a certain fraction of the total number of collisions. It is our purpose in this paper to show how the influence of exchange can be ascertained in such cases by considering the statistical weights of the various molecules. In particular we shall deal with the coefficients of viscosity, heat conduction and diffusion, giving explicit calculations for hydrogen and neon.

I. VISCOSITY

We require first a knowledge of the effect of symmetry in the special case of a gas composed entirely of indistinguishable molecules. Such a gas will be said to consist of *similar* molecules. We imagine a second gas to consist of dynamically equivalent but *dissimilar* molecules, i.e., molecules which are mutually distinguishable. The calculations for these two gases will differ solely in that the wave functions describing collisions between molecules of the first gas must be symmetric in the coordinates of the colliding molecules.

The problem of finding the effect of the symmetry in a gas containing pairs of similar and dissimilar molecules reduces to the problem of finding in what fraction of the total number of molecular encounters the colliding molecules are similar. This fraction will obviously depend on (A) the probability that two molecules selected at random in the gas are similar and (B) the cross section for encounter between these molecules. Through this difference there arise two distinct cross sections for any specified kind of collision between gas particles, *viz.*, Q_S which

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[1] Cf. J. Chem. Phys. **4**, 229 (1936); also Phys. Rev. **51**, 596 (1937).

[2] H. S. W. Massey and C. B. O. Mohr, Proc Roy Soc. **A141**, 434 (1933).

applies to collisions between similar particles, and Q_D which applies to the dissimilar particles. The method of the calculation may be illustrated in the case of the coefficient of viscosity, the formula for which we write (see (12) and (13) below),

$$\eta = C/\int wQdv, \tag{1}$$

in which C is a constant for a given temperature and w is the statistical weight of the cross section Q. The integration is over the relative velocity of the colliding particles.

For the gas under consideration there are two cross sections, *viz.*, Q_D for dissimilar and Q_S for similar molecules. The probabilities that two molecules selected at random are similar and dissimilar shall be denoted respectively by S and D. Thus in place of (1) we may write

$$1/\eta = (1/C)\int (DQ_D + SQ_S)wdv, \tag{2}$$

w now being the classical weighting function. Since D and S do not depend on v, we have

$$1/\eta = D/\eta_D + S/\eta_S \tag{3}$$

in which η_D and η_S represent the coefficients of viscosity respectively of the totally dissimilar and totally similar gases. Using the relation

$$D + S = 1,$$

and setting $\eta_D = (1+\Delta)\eta_S$,

we obtain $\eta = (1+\Delta)/(1+S\Delta)\eta_S. \quad (4)$

It remains to determine S. We shall do this first in the case of hydrogen, in view of the importance of the result for the theory of *ortho*- and *para*-modifications of this gas. Let the gas contain N molecules of which n_J are in the rotational state J. For even J these are paramolecules. There are $2J+1$ states, corresponding to the orientations of the vector J, so that $n_J/(2J+1)$ of the paramolecules are in each of these states. Hence the probability that two paramolecules are in the same specified state is

$$[n_J/(2J+1)N]^2. \tag{5}$$

The probability that two paramolecules are both found in any one of the states is therefore

$$S(p) = \sum\nolimits_J \frac{1}{2J+1}\left(\frac{n_J}{N}\right)^2, \quad J \text{ even.} \tag{6}$$

The corresponding probability for two orthomolecules is

$$S(\sigma) = \tfrac{1}{3}\sum\nolimits_J \frac{1}{2J+1}\left(\frac{n_J}{N}\right)^2, \quad J \text{ odd.} \tag{7}$$

The factor one-third appears in the latter by virtue of the three nuclear spin states which the orthomolecules possess at all temperatures. The n_J/N depend on the concentrations of ortho- and parahydrogen and on the Boltzmann factors corresponding to the values of J and the temperature.

In Table I the dependence of the coefficient of viscosity on the parahydrogen content at several temperatures is shown by values of

$$\frac{\eta - \eta_S}{\eta_S} \cdot 100 = \left(\frac{1-S}{1+S\Delta}\right)\Delta \cdot 100, \tag{8}$$

in which η is the coefficient of viscosity for the concentration of parahydrogen indicated in the table. $\Delta \cdot 100$ is taken from Table II and the quantity S is given by

$$S = S(p) + S(0). \tag{9}$$

The formula for the Boltzmann factor n_J is

$$n_J = N\frac{g_J \cdot e^{-E_J/kT}}{\sum_J g_J \cdot e^{-E_J/kT}}. \tag{10}$$

It is to be observed from the first column of Table I that when the gas is pure parahydrogen an effect of dissimilarity is present. It will be seen that this dissimilarity becomes appreciable at ordinary temperatures causing the viscosity of pure parahydrogen at 273°K to differ from that of a gas of entirely similar particles by 3.3 percent.

We shall now turn to the quantum-mechanical evaluation of the cross sections required in the theoretical calculation of the coefficients of

TABLE I. *Percentage differences between the viscosities of actual hydrogen and an ideal gas of purely similar particles.*

ABSOLUTE TEMPERATURE	PERCENTAGE OF PARAHYDROGEN			
	100	95	43	25
273	3.3	3.5	4.7	4.9
170	2.3	2.7	5.6	6.0
90	0.2	0.7	5.8	6.5
70	0.1	0.8	5.9	6.7

viscosity η_S and η_D. As is shown in the paper of Massey and Mohr, the collision cross section effective in viscosity is given by

$$Q_\eta=\frac{4\pi}{k}\sum_{n=0}^{\infty}\left\{\frac{4n^3+6n^2-2n-2}{(2n-1)(2n+3)}\cdot\sin^2\delta_n\right.$$
$$\left.-\frac{2(n+2)(n+1)}{2n+3}\cos(\delta_n-\delta_{n+2})\sin\delta_n\sin\delta_{n+2}\right\},\tag{11}$$

in which $k=Mv/2h$, M is the mass of the molecule, v the relative velocity in collision, and the δ_n are the phases of the wave functions of the scattering. When the molecules are similar the phases of odd order are omitted in the summation which is then multiplied by two. These cross sections are related to the coefficient of viscosity by Chapman's formula,[3]

$$\eta=\frac{5}{4M^2j^3}\left(\frac{2\pi}{Mj}\right)^{\frac{3}{2}}\cdot\frac{1+\epsilon}{R}.\tag{12}$$

Here $j=1/2kT$, k is Boltzmann's constant, and

$$R=\tfrac{1}{2}\int_0^\infty v^7Q_\eta\cdot e^{-\frac{1}{2}jMv^2}dv.\tag{13}$$

The quantity ϵ involves the interaction of the molecules, but as it does not exceed 0.017 in classical theory, its quantum theory correction is unnecessary. We are here interested not in the absolute value of the viscosity but the changes in it due to exchange. We shall base all numerical work on the hard sphere model of the molecule as this model allows exact determination of the phases δ_n. It will be seen that the model gives values of η which, except at low temperatures, are in sufficient accord with experiment for present purposes. Approximate estimates of Q_η for central forces between the molecules show that, as long as many phases enter the summation, the exact nature of these forces has small effect on the ratio of the values of Q_η for similar and dissimilar particles. To demonstrate this we may write (11) approximately

$$Q_\eta\backsimeq\frac{4\pi}{k^2}\sum_{n=0}^{\infty}\{(n+\tfrac{1}{2})\sin^2\delta_n$$
$$-(n+\tfrac{3}{2})(\sin^2\delta_n\sin^2\delta_{n+2}$$
$$+\tfrac{1}{4}\sin 2\delta_n\sin 2\delta_{n+2})\}\tag{14}$$

and make use of the rapid variation of the phases in the region δ_0 to $\delta_m\sim\frac{1}{2}$ by assigning to $\sin^2\delta_n$, $\sin^2\delta_{n+2}$ and $\sin 2\delta_n$ average values $\frac{1}{2}$, $\frac{1}{2}$ and zero. Thus the contributions to the cross sections from this range of the summations are:

$$\frac{\pi}{k^2}\sum_0^m(n-\tfrac{1}{2})\backsimeq\frac{\pi m^2}{2k^2}\tag{15}$$

for dissimilar particles, and

$$\frac{2\pi}{k^2}\sum_0^{m/2}(2n-\tfrac{1}{2})\backsimeq\frac{\pi}{2k^2}(m^2+m)\tag{16}$$

for similar particles. To obtain the terms of the summation for $n>m$ it is necessary to know the δ_n. For an attractive central field with potential $V=-D/r^S$ Massey and Mohr[4] have calculated the phases using Jeffreys' approximation. Replacing summations over $n>m$ by integrations and letting $\sin\delta_n=\delta_n$ one gets for either the similar or dissimilar particles the contribution

$$\frac{\pi}{2k^2}\frac{m^2}{S-2}\tag{17}$$

to the cross section. This expression is obtained by neglecting the coefficients of $(n+3/2)$ in (14) and therefore should represent an upper limit for the effect ascribable to the special form of the field. For the ratio of similar and dissimilar cross sections we have

$$\frac{Q_\eta(S)}{Q_\eta(D)}=1+\frac{S-2}{S-1}\frac{1}{m}.\tag{18}$$

As a test of this approximation a potential $V=-6.04\times 10^{-60}/r^6$ for hydrogen was used to compute the ratio for a particular velocity. The value given by (11) using phases of Jeffreys' approximation was 1.075 whereas (18) gave 1.064. The corresponding exact value for the hard sphere is 1.080 for which (18) gives 1.087. We see from the foregoing estimate that the differential effect calculated under unfavorable assumptions amounts to 1.1 percent while the hard sphere model gives 0.7. Our assumptions are the more unfavorable since we did not try to fit the field to the observed viscosity and since

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[3] S. Chapman, Phil. Trans. **216A**, 279 (1915).

[4] H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. **A144**, 202 (1934).

the averaging effect and the dropping of the term proportional to $(n+3/2)$ only tends to accentuate the effect based on the first calculation.

If σ is the diameter of the hard sphere, the classical value of Q_η is $2\pi\sigma^2/3$. The quantum theory values of Q_η are always somewhat larger, becoming largest as $v \rightarrow 0$ and tending to the classical value in the limit $v \rightarrow \infty$. Over the range from 3 to ∞ of the parameter $\kappa\sigma$ the values of Q_η may be represented by

$$Q_\eta = \frac{2\pi}{3}\sigma^2\left\{1+\frac{a}{k\sigma}+\frac{b}{(k\sigma)^2}\right\}, \tag{19}$$

in which $a=2.10$, $b=1.50$ for similar particles and $a=1.00$, $b=4.00$ for dissimilar particles. This formula has been obtained by a least square fitting of the constants a and b to tables of Q in the range of $\kappa\sigma$ from 3 to 30. We are not justified in using the hard sphere for $k\sigma<3$ since in this region only a few phases contribute to Q_η which is then sensitive to the field of the molecule. In the case of hydrogen this implies that our calculations become unreliable at temperatures lower than about 70°K. For other molecules the corresponding temperatures are somewhat lower.

Putting (19) in (13) and integrating, we obtain finally

$$\eta = \eta_c\left\{1+\frac{5a}{16}\frac{\hbar}{\sigma}\left(\frac{\pi}{MkT}\right)^{\frac{1}{2}}+\frac{b}{3}\left(\frac{\hbar}{\sigma}\right)^2\frac{1}{MkT}\right\}^{-1}, \tag{20}$$

in which

$$\eta_c = \frac{5}{16}\left(\frac{MkT}{\pi}\right)^{\frac{1}{2}}\frac{1.016}{\sigma^2} \tag{21}$$

is Chapman's classical formula for the coefficient of viscosity based on the hard sphere model.[3]

In Table II are shown values of (18) in micropoise for a hard sphere model of diameter 2.75A and mass equal to that of the hydrogen molecule. η_D is for dissimilar particles and η_S for similar particles. In the last column the quantity in which we are interested is defined by $\Delta = (\eta_D - \eta_S)/\eta_S$.

TABLE II. *Theoretical viscosities of gases composed of dissimilar molecules* (η_D) *and similar molecules* (η_S).

ABSOLUTE TEMPERATURE	EXPERIMENTAL VALUE OF FOR HYDROGEN	η_D	η_S	$\Delta\cdot 100$
273.1	84.2	77.8	73.8	5.4
170.2	60.9	60.0	56.2	6.8
89.6	39.2	41.6	38.7	7.5
70.9	31.9	36.2	33.6	7.7

II. THERMAL CONDUCTIVITY AND VISCOSITY

We have not been able to find in the literature experimental data giving information about the relative viscosity of different mixtures of ortho- and parahydrogen at temperatures of interest. The effect expected by us is comparatively large and should be easy to detect. We are, on the other hand, of the opinion that the effect already has been observed in a somewhat indirect manner but that the data which contain it have not yet been properly evaluated. We are referring to measurements of the thermal conductivity of ortho- and parahydrogen at different temperatures; these observations can be linked up by a simple theoretical reasoning with the viscosity calculations presented above.

A method for determining the *ortho-para* concentration in hydrogen has been based on measurements of the heat given up in a thermal conductivity cell.[5] In this method a wire heated by a constant current passes through the cell containing the hydrogen. The walls of the cell are maintained at lower temperature than the wire. The temperature reached by the wire depends on the conductivity of the surrounding gas. If i is the current in wire and r its resistance at temperature T, then it may be shown that the heat given up per second by the wire is

$$i^2 r = A\int_{T_0}^{T}\lambda dT, \tag{22}$$

A being a geometrical constant for the cell, T_0 the wall temperature and λ the coefficient of thermal conductivity of the gas. Examination of Chapman's theory of heat conduction shows that the formula

$$\lambda = \frac{1}{M}(3.75R + C^{\text{rot.}})\cdot\eta \tag{23}$$

is corrected for quantum theory through the corrections of the rotational specific heat $C^{\text{rot.}}$

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[5] K. F. Bonhoeffer and P. Harteck, Naturwiss. **17**, 182 (1929).

and η. In the formula R is the universal gas constant and M the molecular weight of the gas. Observations of λ therefore should give us information about η and thereby offer verifications of our theoretical predictions.

Since the rotational specific heat is greater in parahydrogen, it is expected that λ for this gas should be greater than for orthohydrogen and consequently the temperature reached by the wire in the thermal conductivity cell should decrease with increasing parahydrogen content of the inclosed gas. It may be seen from Table I that the variation in viscosity will tend to offset this change. For temperatures which have been investigated experimentally the effect due to the specific heat has preponderated, although we shall show that in certain temperature ranges the viscosity may become the more important factor thus causing an increase in T with increase in *para*-H_2 concentration. It is to be observed that, while the change in T due to that in $C^{\mathrm{rot.}}$ will depend linearly on the percentage of parahydrogen present, the change in T due to η is not linear with respect to this percentage. An experimental test[6] was made to confirm the linear dependence of T on the parahydrogen content, but as this test was confined to *para*-H_2 concentrations less than 48 percent, it did not involve the region (see Table II) in which there are large and nonlinear variations of η.

Table III shows data obtained with thermal conductivity cells which may be analyzed to show the presence of variation in η due to change in *para*-H_2 concentration. In every case the walls of the cell were maintained at the temperature of liquid hydrogen.

The ratio of the heat given up in the cell when filled with hydrogen of given parahydrogen concentration to that given up when it is filled with normal hydrogen (25 percent *para*-H_2) is by (22) and (23)

$$\frac{r'}{r}=\frac{\displaystyle\int_{T_0}^{T'}(3.75R+C'^{\ \mathrm{rot.}})\eta' dT}{\displaystyle\int_{T_0}^{T}(3.75R+c^{\mathrm{rot.}})\eta dT},$$

where the unprimed quantities refer to the normal hydrogen. Let $\eta'=\eta(1-z)$ over the range of integration T_0 to T' and assume $\eta\propto T^{\frac{3}{4}}$. Then the last expsession may be written

$$r'/r=(1-\bar{z})I'/I, \tag{24}$$

where
$$I=\int_{T_0}^{T}(3.75R+C^{\mathrm{rot.}})T^{\frac{3}{4}}dT, \tag{25}$$

and $\bar{z}$ is the value of z averaged with respect to the integrand of I. The assumption $\eta\propto T^{\frac{3}{4}}$ for the computation is made because the empirical values of the thermal conductivity of normal hydrogen are best represented by this variation in η. The values of $\bar{z}$ are insensitive to choice of the law of this variation provided the latter is between $\eta\propto T^{\frac{1}{2}}$ and $\eta\propto T$. The value $\bar{z}=0$ would correspond to identity of the viscosity coefficient for ortho- and parahydrogen.

In Table IV the third and fourth columns show, respectively, the values of $\bar{z}$ computed directly with (24) from the data of Table III and computed according to the present theory for the variation of η using the values shown in Table I. The fact that $\bar{z}$ is different from zero reduces the influence of the difference of the specific heat of the ortho and para modifications to almost $\frac{1}{2}$ in the first observation.

As already remarked, the thermal conductivity of parahydrogen is greater than that of orthohydrogen, owing to the greater rotational specific heat of the former. The viscosity tends to reduce this difference. On the basis of the values given in Table I it is found that the conductivities of the two modifications should become equal at about 80°K and at lower temperatures the conductivity of the orthohydrogen should be the greater.

TABLE III. *Data on thermal conductivity which may be analyzed to show a variation in η due to parahydrogen concentration.*

PERCENTAGE OF PARAHYDROGEN	RESISTANCE OF CELL WIRE IN OHMS	TEMPERATURE OF WIRE °C	AUTHORITY
25	111.85	203.9	*A*
99.7	106.27	191.6	
25	135.3	173.0	*B*
43	134.0	170.0	

(*A*) Bonhoeffer and Harteck.[5]
(*B*) Farkas.[6]

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[6] A. Farkas, Zeits. f. physik. Chemie **B10**, 419 (1930).

Effects of symmetry of the kind that have been discussed above for hydrogen will be present in the modifications of deuterium. The effects will be very much smaller in magnitude, mainly because of the multiplicity of nuclear spin states which exist for either of the modifications. The deuteron has spin unity and there are consequently 3 nuclear spin states for the para- and 6 for the orthodeuterium. The expressions for $S(p)$ and $S(o)$ will be correspondingly reduced making the number of collisions of *similar* molecules too few to produce appreciable effects. Moreover, since the total effect of the symmetry depends nearly inversely on the square root of the mass of the molecule, there will be a reduction in the case of D_2 due to its larger mass.

In the foregoing consideration the contribution of inelastic collisions to the viscosity has not been taken into account. Apart from the fact that no simple general rule can be given for the symmetrization of the wave function in processes where the internal condition of the system is changed it should be remembered that these inelastic collisions become of negligible importance at low temperatures where the calculated effects become marked.

III. THE COEFFICIENT OF DIFFUSION

The theoretical derivation of the coefficient of diffusion is usually presented in analogy with the derivation of viscosity or thermal conductivity coefficients but needs modification as far as the symmetry properties are concerned. Massey and Mohr have symmetrized the wave functions in the calculation of the coefficient of diffusion in the same way in which they symmetrized them for obtaining viscosities. They therefore obtained curves for the coefficient of diffusion of similar and dissimilar particles (coefficient of self-diffusion). In our opinion no symmetrization has to be used for the calculation of the coefficient of diffusion or even "self-diffusion." Our reasons are as follows:

TABLE IV. *Values of $\bar{z}$, measure of variation of coefficient viscosity with ortho para concentration, as calculated directly from the data of Table III and as computed from the present theory.*

PERCENTAGE OF PARAHYDROGEN	I'/I	r'/r	$\bar{z}$ from (24)	$\bar{z}$ from theory
100	1.010	0.946	0.063	0.050
43	0.993	0.988	0.005	0.006
25	1.000	1.000	0	0

The processes of diffusion of two gases consist in the change with time of the relative composition of the gases at different parts of space. For this process of diffusion collisions between identical molecules are immaterial because they do not lead to mass transport in toto. Only if the particles contained in the gas show some feature by which they can be distinguished can there be any meaning ascribed to the term diffusion. By self-diffusion in the classical theory a process was understood in which particles of almost identical physical properties (e.g. isotopes) exchange places with each other. This example alone shows that there cannot be any justification for symmetrization of the wave function since isotopes obviously are not identical particles. If on the other hand the particles are identical in every respect then no diffusion process can occur.

To make this even more clear we consider the microscopic description of the phenomena using wave functions of all particles in the gas instead of the macroscopic description which refers only to densities of the particles. Any state of the gas composed at N particles of which n_i might all be identical among each other and said to belong to the ith sort will then be described by a wave function in the $3N$ dimensional configuration space; the wave function will be symmetrical (or anti-symmetrical) with respect to permutations of each of the n_i particles in each sub-group among each other. Forces between the particles will determine the collisions and also the change with time of the wave function. The symmetrization refers only to the sub-group but interactions between these particles do not change the relative composition as far as two sub-groups are concerned.

We therefore conclude that there is no place in the process of diffusion for the symmetrization of the wave functions and that the curve which was obtained by Massey and Mohr by symmetrization and which differs from the classical curve even in the limit of infinitely small wavelengths lacks physical significance.

IV. VISCOSITY OF A GASEOUS MIXTURE—APPLICATION TO NUCLEAR SPINS OF ISOTOPES

Application of the ideas presented in the preceding paragraphs to other gases besides hydrogen will only in exceptional cases lead to experimentally discoverable results. The reason for this is to be found in the fact that most of the gases at temperatures which allow convenient experimentation are generally composed of particles (atoms and molecules) in so many different states that interaction by similar particles becomes comparatively a rare event. This holds true primarily for molecular gases (apart from hydrogen) where due to the many rotational states present the best approximative description could be obtained by not symmetrizing the wave function. Monatomic metallic vapors would be more promising but they mostly allow observations only at so high temperatures that due to the small wave-length the symmetrization effect becomes unimportant. Many of them furthermore possess an electronic, orbital or spin angular momentum which leads to a weight factor $2J+1$ increasing the percentage of "dissimilar particles." Their high mass also makes experimentation with them disadvantageous.

The noble gases are in an exceptional position in that they are free of rotational states and have a singlet electronic term in the ground state. The only degeneracy which therefore can arise is due to a possibly present nuclear spin. We shall show that measurements of viscosities of noble gases with varying isotope content will give information about the nuclear spin of the isotopes. It is important to point out that this information is completely independent of the magnetic nuclear moment which might be associated with the nuclear spin. The method can therefore be applied even if this magnetic moment should be too small to give hyperfine structure splitting.

For a gaseous mixture of two components, Chapman[7] gives the formula for the coefficient of viscosity,

$$\eta_{12}=\frac{5kT}{\pi K_{12}^{(2)}}\cdot\frac{a\nu_1^2+2b\nu_1\nu_2+c\nu_2^2}{a'\nu_1^2+2b'\nu_1\nu_2+c'\nu_2^2},\qquad(26)$$

where ν_1 and ν_2 are the concentrations of the two gases. The coefficients are given by:

$$a=1+\frac{3}{10}\frac{m_1}{m_2}\frac{K_{12}^{(2)}}{K_{12}^{(1)}},\quad c=1+\frac{3}{10}\frac{m_2}{m_1}\frac{K_{12}^{(2)}}{K_{12}^{(1)}},$$

$$a'=\frac{K_{11}^{(2)}}{K_{12}^{(2)}}\cdot a,\qquad c'=\frac{K_{22}^{(2)}}{K_{12}^{(2)}}\cdot c,$$

$$b=1-\frac{3}{10}\frac{K_{12}^{(2)}}{K_{12}^{(1)}}+\frac{3}{40}\frac{(m_1+m_2)^2}{m_1m_2}\frac{K_{11}^{(2)}+K_{22}^{(2)}}{K_{12}^{(1)}},$$

$$b'=1+\frac{3}{40}\frac{(m_1+m_2)^2}{m_1m_2}\frac{K_{11}^{(2)}K_{22}^{(2)}}{K_{12}^{(1)}K_{12}^{(2)}},$$

$$K_{ij}^{(t)}=\frac{8}{\pi t}\left\{\frac{(m_i+m_j)2kT}{\pi m_im_j}\right\}^{\frac{1}{2}}\int_0^\infty y^{2(t+1)+1}\cdot e^{-y^2}Q_{ij}^{(t)}dy\qquad(27)$$

and

$$Q_{ij}^{(t)}=\pi t\int_0^\infty(1-\cos^t\theta_{ij})pdp.\qquad(28)$$

In these expressions the m's are the masses of the molecules,

$$y=\left\{\frac{m_im_j}{(m_i+m_j)2kT}\right\}^{\frac{1}{2}}v_{ij},$$

v_{ij} is the relative velocity, θ_{ij} the angle turned through by this velocity in collision, and p is the perpendicular distance between the asymptotes of the orbits of the colliding particles. The quantities affected by exchange are the $Q_{ij}^{(t)}$ which represent cross sections. For $t=1$ these are the "cross sections effective in diffusion." Quantum theory values for the hard sphere have been given by Massey and Mohr.[2] The question of exchange does not arise for these cross sections and the corrections due to quantum theory are negligible except for light elements at low temperatures. For $t=2$ the $Q_{ij}^{(2)}$ take the form of the "cross sections effective in viscosity" and are represented for the hard sphere by (19); the effect of symmetry being accounted for by the values assigned to a and b. As the colliding molecules can only be identical when they are of equal mass the exchange influences the $K_{ii}^{(2)}$ alone, and it follows from the form of the latter that they may be expressed

$$K_{ii}^{(2)}=D_iK_{ii}^{(2)}(D)+S_iK_{ii}^{(2)}(S),\qquad(29)$$

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[7] S. Chapman, Phil. Trans. **217A**, 115 (1916).

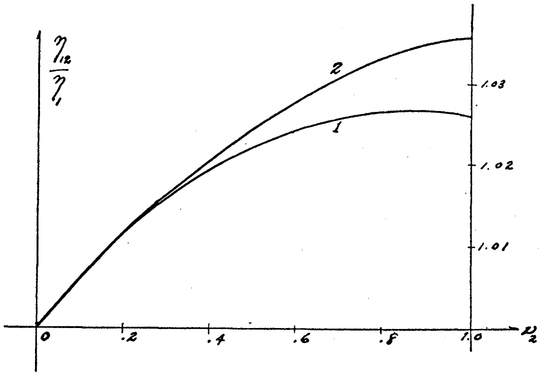

FIG. 1. Viscosity of a mixture of the isotopes of neon 20 and 21 relative to neon 20. The abscissa gives the concentration of neon 21. Curves 1 and 2 correspond respectively to the assumptions that neon 21 has nuclear spin 0 and $\frac{1}{2}$.

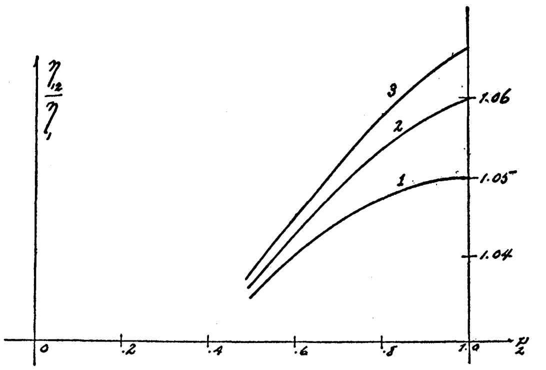

FIG. 2. Viscosity of a mixture of the isotopes of neon 20 and 22 relative to neon 20. The abscissa gives the concentration of neon 22. Curves 1, 2 and 3 correspond respectively to the assumptions that neon 22 has nuclear spin 0, $\frac{1}{2}$ and 1.

where D_i and S_i have the meanings given them in the discussion of a simple gas, and $K_{ii}^{(2)}(D)$, $K_{ii}(S)$ are obtained by using the appropriate cross sections Q_D, Q_S.

We shall now apply these results numerically to the isotopes of neon which, as mentioned, should allow of experimental verification and offer information as to the spin of the nucleus. In a mixture of the neon isotopes of atomic weights 20 and 21 we may assume neon 20 has zero nuclear spin and therefore the neon 20 atoms are identical among themselves so that in (29) we will have:

$$S_1=1, \qquad D_1=1-S_1=0,$$

since only the nuclear spin states will be present at ordinary temperatures. The diameters of the isotopes may be taken equal. With spin i_2 for the neon isotope 21 we will have:

$$S_2=1/(2i_2+1), \qquad D_2=2i_2/(2i_2+1).$$

In Fig. 1, corresponding to a temperature of 0°C and atomic diameter 2.55A, curves based on the above formulae (19), (26), (27), (28), are drawn to represent the coefficient of viscosity of the mixture of the neon isotopes 20 and 21 relative to neon 20. Curves 1 and 2 are based on the assumptions of 0 and $\frac{1}{2}$ for the nuclear spin of neon 21. In Fig. 2 analogous curves are given for a mixture of the neon isotopes 20 and 22; the curves 1, 2 and 3 are respectively for spins 0, $\frac{1}{2}$ and 1 for neon 22. Our knowledge of the constitution of nuclei leads us to expect the spin of zero or possibly unity. The curve referring to spin $\frac{1}{2}$ is shown for illustrative purposes. For the isotopes of argon the effect will be reduced due to both the larger mass and radius of the argon atom. Approximately (as may be seen from (19)), the total effect due to symmetry varies inversely as the molecular diameter and inversely as the square root of the mass of the molecule. The effect in the case of neon is susceptible to test by any of the standard experimental methods of measuring relative viscosities inasmuch as these methods easily secure an accuracy somewhat better than 1 part in 1000.